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ESTABLISHMENT OF NATIONAL EMISSION STANDARDS FOR STATIONARY SOURCES. VOLUME V. NITRIC ACID PLANTS

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ESTABLISHMENT OF NATIONAL EMISSION STANDARDS FOR STATIONARY SOURCES

Volume V Nitric Acid Plants

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TABLE OF CONTENTS

		Page No.
1.0	INTRODUCTION	1
2.0	PROCESS DESCRIPTION	2
	2.1 Pressure Process	2
	2.2 Other Processes	4
	2.3 Power Recovery	5
3.0	EMISSIONS	6
	3.1 Nitrogen Oxides	6
	3.2 Acid Mist	6
	3.3 Visible Emissions	8
4.0	CONTROL TECHNIQUES CURRENTLY USED FOR NITRIC ACID PLANTS	8
	4.1 Plant Design and Operation	9
	4.2 Catalytic Combustion	9
	4.3 Other Control Techniques	13
	4.4 Control Costs	14
5.0	PLANTS CURRENTLY USING BEST TECHNOLOGY	17
6.0	CURRENT REGULATIONS LIMITING NO_x EMISSIONS FROM NITRIC ACID PLANTS	18
7.0	RECOMMENDED EMISSION LEVELS FOR NEW PLANTS	19
	REFERENCES	20

EMISSION STANDARDS FOR NITRIC ACID PLANTS

1.0 INTRODUCTION

In 1968, an estimated 9,600,000 tons of nitrogen oxides (NO_x, expressed as NO_2) were emitted from stationary sources. The vast majority of this emission resulted from the high temperature fixation of atmospheric nitrogen and oxygen during combustion of coal, oil, and gas, and the combustion of gasoline and diesel fuel in stationary internal combustion engines.[1] The manufacture of nitric acid generated emissions of approximately 150,000 tons of NO_x in 1968 or about 1.6% of the total NO_x emitted from stationary sources.[2] There were approximately 72 nitric acid manufacturing establishments in the United States in 1968 with a total capacity of 7.7 million tons of acid per year.[3]

Though emissions from nitric acid plants do not account for a major proportion of NO_x on a nationwide basis, large individual plants can be large point sources of this pollutant. A large, well operated modern plant producing 500 tons per day (tpd) of nitric acid[a] will emit approximately 175,000 pounds of tail gas per hour containing about 1,000 pounds of NO_x at a concentration of 3,000 ppm by volume.[4] This emission rate is equal to 12.0 tons of NO_x per day. Approximately 50% of this emission will usually be in the form of nitrogen dioxide, a very visible reddish-brown colored gas. Most new plants utilize catalytic combustion devices to decrease operating costs and to reduce NO_x emissions.

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a Plant capacities are always expressed in tons of equivalent 100% strong nitric acid. Acid actually produced is approximately 56-60% strong.

2.0 PROCESS DESCRIPTION

2.1 Pressure Process

Almost all nitric acid in the United States is manufactured by the high pressure, ammonia oxidation process, and all new plants for the production of unconcentrated acid are of this type. In this process, shown in Figure 1, air and ammonia are preheated, mixed in a ratio of about 9:1, and passed over a platinum-rhodium catalyst. The following reaction occurs:

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O \qquad (1)$$

This reaction is approximately 95% to 98% complete. The stream is cooled to 100°F or less, and the nitric oxide (NO) reacts with more oxygen to form nitrogen dioxide and its liquid dimer, nitrogen tetroxide.

$$2NO + O_2 \longrightarrow 2NO_2 \rightleftharpoons N_2O_4 \qquad (2)$$

The liquid and gas then enter a bubble-cap absorption tower. Additional air is added to the bottom of the tower, and water to the top. The NO_2 (or N_2O_4) reacts exothermically with water to form nitric acid and NO, as follows:

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO \qquad (3)$$

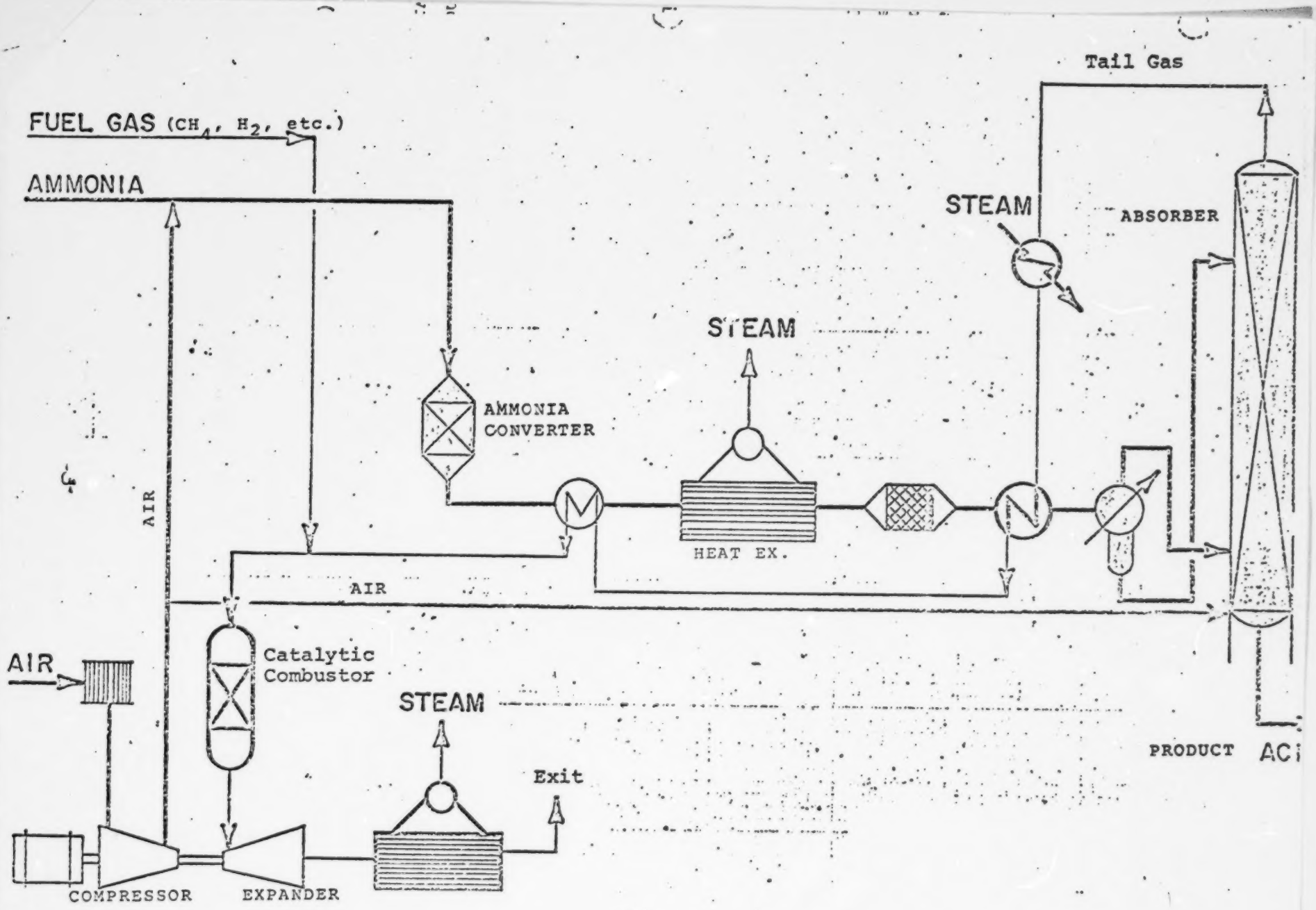

FIGURE 1. NITRIC ACID PRODUCTION PROCESS

The formation of one mole of NO for every 2 moles of HNO_3 makes it necessary to reoxidize NO after each absorption stage, and limits the overall level of recovery that can be economically achieved.

Acid product is withdrawn from the bottom of the tower in concentrations of 55% to 60%. The air entering the bottom of the tower serves to strip NO_2 from the product and supplies oxygen for reoxidizing the NO formed in making nitric acid.

Normally, pressures of 100 to 120 psig are employed in the oxidation and absorption operations. Tail gas from the absorber passes through a mist eliminator and is then reheated by exchange with the hot gases from ammonia oxidation. To recover energy, the tail gases are passed through a turbo expander.

2.2 Other Processes

Before corrosion resistant materials were developed, the ammonia oxidation and absorber operations were carried out at essentially atmospheric pressure in stoneware reactors. Because of the low absorption and NO oxidation rates, much more absorption volume was required, and several large towers were placed in series. A few of these low-pressure units are still in operation, but they represent less than 5% of the current United States nitric acid capacity. Improved technology has made the "pressure process" more economical, and it is currently the preferred process in the United States.

Variations in the nitric acid pressure process exist in the United States, but they account for only a small percentage of overall production. These variations apply

mainly to the pressure used in the process. In the combination pressure process, the ammonia oxidation occurs at essentially atmospheric pressure, and the oxidation products are compressed to 50 to 60 psig before absorption.

2.3 Power Recovery

Among the largest potential operating costs in nitric acid production is the power required to compress the air used in the oxidation and absorption steps. To off-set this large operating cost, the tail gas from the absorption system which is still at a high pressure is heated by heat exchange with other gas streams, and the energy in this gas is used to help drive the air compressor. In older plants with reciprocating compressors, about 40% of the power was obtained from this tail gas expansion.[5]

More recent plants, equipped with centrifugal or turbine type compressors have heated the tail gas to higher temperatures by passing it through a catalytic combustor. This combustor raises the tail gas temperature up to approximately 1300°F and thus provides additional available power recovery.

Modern well designed plants can operate with complete power recovery and can also export steam to other nearby plant processes.[5,6] The incorporation of catalytic combustion devices in modern plants has also provided a reduction in the type and quantity of NO_x emitted to the atmosphere, as described in later sections of this report.

3.0 EMISSIONS

3.1 Nitrogen Oxides

Nitrogen oxide emissions consist mainly of NO and NO_2, and are emitted to the atmosphere from the absorber tail gas stream after it leaves the expander and final heat exchangers. These emissions vary with the plant design, and maintenance, production rate, and absorber efficiency. Absorber efficiency can be increased by higher pressures and low temperatures, and result in lower NO_x emissions.

Emissions of NO_x from well maintained and properly operated nitric acid plants without catalytic combustion devices are generally in the 2000 to 4000 ppm range (equal to 32 to 64 pounds of NO_x per day per ton of acid produced on a 100% basis). However, emissions as low as 1000 ppm have been reported.[7,8]

Plants equipped with catalytic combustion devices which are operated mainly for energy recovery reduce the NO_2 content of the tail gas to levels of 50 to 200 ppm as evidenced by their colorless exit gas stream. However, the NO content of these streams is usually between 400 and 3500 ppm.[6,4]

3.2 Acid Mist

Acid mist emissions do not occur from a properly operated plant. Acid mist is present in the gases leaving the absorber. However, these are largely removed by either cyclone type or mesh mist collectors before these gases are heated by heat exchange prior to entering the catalytic combustor or turbo expander.[9] Trace quantities of acid mist present in the tail gas are vaporized as the gas is re-heated.

Table 1 presents typical tail gas compositions found in modern well operated plants.

TABLE 1. Typical Ranges of Nitric Acid Plant Tail Gas Composition, Temperature and Pressure.

	Absorber Exit	Catalytic Combustor Inlet	Outlet
% NO	0.10-0.20	0.10-0.20	0.04-0.35
% NO_2	0.10-0.20	0.10-0.20	0 - .03
% O_2	2 to 4	2 to 4	0 -1.5
Temp. °F	90-100	800-1000[a]	1000- 1300
Pressure, psig	85-95	80-90	75-90[b]

a) When using methane or propane as auxiliary fuel. A lower temperature can be used for fuels with more hydrogen.

b) Depends on type of catalyst, i.e. honeycomb or pellet.

3.3 Visible Emissions

Visible emissions of a reddish-brown color occur from all existing nitric acid plants without catalytic combustion due to the NO_2 present in the exit gas. NO is an invisible gas; however, it oxidizes to NO_2 in the atmosphere. Under poor atmospheric ventilation conditions, such as low wind speeds and inversion conditions, the oxidized NO in the ambient air may form a faintly visible reddish cloud.

The opacity of this visible emission varies with the NO_2 content of the exit gas stream and the stack diameter. The visible threshold concentration of NO_2 on a ppm by volume basis is approximately given by the equation:

$$Co = \frac{2400}{d}$$

Where, d = stack diameter in inches and Co = visible concentration, ppm.[10] Thus for a twelve-inch diameter exit stack, a visible emission would occur at an NO_2 concentration of approximately 200 ppm (2400/12). Plants with large diameter stacks would thus require better control techniques to prevent a visible plume.

4.0 CONTROL TECHNIQUES CURRENTLY USED FOR NITRIC ACID PLANTS

Emissions of nitrogen oxides can be reduced to very low levels by utilizing good plant design, proper operation and maintenance, and the use of emission reduction devices such as catalytic combustors.

4.1 Plant Design and Operation

Good plant design requires adequate compressor capacity to maintain the high pressures in the absorption tower, and also to provide sufficient oxygen for the oxidation of NO to NO_2 in the absorption tower. Adequate cooling of the absorption tower is also required to remove the heat of reaction and thus increase absorption rates. This cooling is accomplished by passing cold water through cooling coils in the absorber. The availability of a cold supply of water is an important factor in efficient absorper operation; especially in warm climates. Current plant design practices limit for economic reasons, the NO_x concentration in the tail gas to about 2,000 ppm.[12]

Proper operation requires operating the plant at design rates in regard to production and product acid concentration. Strict maintenance of the various high pressure lines, especially the heat exchangers, is also required to prevent high concentrations of NO_x from entering the atmosphere. Leaks in the shell and tube type heat exchangers can cause gas streams containing 8 to 9% NO_x to flow into the tail gas stream, thus significantly increasing the tail gas NO_x emissions. Routine measurements of the gas streams will indicate process leaks.

4.2 Catalytic Combustion

Due to the energy recovery requirements in an economically operated nitric acid plant, catalytic combustors are used on all new plants. In these devices, the absorber tail gas is heated to the necessary catalyst ignition temperature, mixed

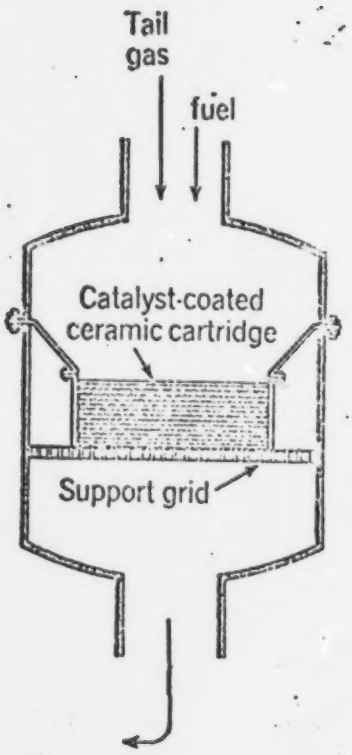

Figure 2. Typical Catalytic Combustion Unit

with fuel such as natural gas, propane, or ammonia purge gas, and passed over the catalyst bed. A typical catalytic combustor unit is shown in Figure 2. A number of reactions take place resulting in increased gas temperature, and the dissociation and decomposition of NO_x. The following reactions using methane as the fuel illustrate the major reactions:

$$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O \qquad (4)$$

$$CH_4 + 4\ NO_2 \longrightarrow 4\ NO + CO_2 + 2\ H_2O \qquad (5)$$

$$CH_4 + NO \longrightarrow 2\ N_2 + CO_2 + 2\ H_2O \qquad (6)$$

Reactions (4) and (5) proceed rapidly, with evolution of considerable heat. Since the nitrogen dioxide is all converted to nitric oxide in reaction (5), the gas is now colorless even though there is yet no substantial destruction of nitric oxide. The reaction of further amounts of natural gas with the nitric oxide in accordance with reaction (6), which takes place more slowly, results in decomposition of the nitric oxide to nitrogen. When this reaction is complete, essentially total abatement is achieved.

Usually the catalyst consists of 0.5 percent platinum or palladium on a support such as woven Nichrome ribbon or ceramic material having a pelleted or honeycomb structure. The honeycomb support offers the advantage of low pressure drop. The catalyst will withstand temperatures as high as 1,400 to 1,500°F, which is also the approximate upper temperature limit for the reaction vessels used in this service.

Space velocities of about 100,000 $ft.^3/hr$ per $ft.^3/catalyst$ are used for honeycomb catalysts and about 30,000 for pelletized catalyst.[13,14]

Temperature rise is a critical factor in achieving fairly complete elimination of NO_x. Total temperature rise is very dependent on the oxygen content of the incoming gas stream. Initial ignition temperature is determined by the type of fuel and the type of catalyst. With natural gas fuel, temperatures in the 900-950°F range are required for ignition, and the temperature rise is about 270°F for each percent oxygen in the tail gas.[15] A combustor exit temperature of about 1600°F would be required for essentially complete reduction of NO_x.[a]

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a Based on 2.5% O_2 in the tail gas.

With hydrogen fuel, the ignition temperature is much lower - about 290°F, and the temperature rise is about 300°F for each percent oxygen in the tail gas.[15] An exit temperature of about 1000°F is thus required for essentially complete reduction of NO_x[a].

Nitric acid plants which can utilize ammonia plant purge gases (60% H_2, 15% CH_4, and some ammonia and inerts) can achieve fairly complete reduction of NO_x in single stage combustors, and maintain exit temperatures on the order of 1200°F. Ammonia plant purge gas is normally a waste stream discharged to the atmosphere.

Because temperature limits the extent of reaction in a single-stage reactor, a two-stage reduction process may be required to split the heat load. This would permit use of excess fuel, or operation on the reducing side, whereby all oxygen in the tail gas is reacted and the nitrogen oxides are decomposed in accordance with equation (6). The stack effluent will contain 0.01 to 0.02 percent or less of total nitrogen oxides. It is technically possible to carry out essentially full reduction and decomposition of the nitrogen oxides (for example, to 0.01 to 0.02 percent NO_x) in a single stage if the oxygen content of the absorber tail gas is kept well below about 3% so as to reduce the heat of reaction.

NO_x reduction efficiencies currently available in catalytic combustion units vary widely. When new, these units operate very well and can reduce NO_x emissions to less than 50 ppm.[16,17] However, continued operation at this level has not been widely achieved especially when using natural gas. This reduction in efficiency appears to be the result of catalyst erosion and poisoning. Trace amounts of sulfur present in the fuel

will poison the catalyst. Catalyst manufacturers do not appear to guarantee their units for more than one year.

To date, the single stage pelletized catalyst units appear to maintain high levels of reduction efficiency (80 to 90%) for longer periods of time. Fuel requirements of 10-20% over stoichiometric are required for high reduction efficiencies.[18] Emissions, when using hydrogen, or ammonia plant purge gas are generally much lower.

Some new plants are currently being designed for emission limits of 200 ppm of total NO_x. Recent requests for proposals by the Corps of Engineers for nitric acid plants specified 100 ppm NO_x in the tail gas, however this limit was later raised to 200 ppm.[19] While this relatively low limit is achievable with sufficient catalyst and fuel, the maintenance of this level may present a problem. Catalyst replacement every 1 or 2 years may be required.

4.3 Other Control Techniques

Both absorption and adsorption techniques can be adapted ~~adopted~~ to reducing NO_x emissions.[18] Scrubbing with alkaline solutions has been practiced at a few plants, but high removal efficiencies are difficult to maintain and disposal of the spent solution may present a problem.

Adsorption on silica gel or molecular sieves has been demonstrated on a small scale, but is not commercially practiced at present.

4.4 Control Costs

Single stage catalytic combustion units suitable for decolorizing the tail gas, for a 500 tpd nitric acid plant cost approximately $100,000.[6] A dual combustor arrangement designed for high efficiency NO_x removal would add between $60,000 to $90,000 to this cost, and a single stage high efficiency unit with final waste heat boiler would cost between $120,000 to $180,000.[12] The total cost of a 500 tpd nitric acid plant is about $4.9 million.[a] Table 2 presents other estimated costs for 2 catalytic control plans.

Operating costs depend on the fuel cost, plant steam requirements and costs, and power recovery. When ammonia plant purge gas is used, the fuel cost is zero. Even when natural gas is used an operating profit may be shown if a demand for steam exists.

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a) Based on a cost of $3.6 million for a 300 tpd plant

$$\left(\frac{500}{300}\right)^{0.6} \times \$3.6 \times 10^6 = \$4.9 \times 10^6$$

Table 2. Estimated Costs of Catalytic Reduction for Two Control Systems[18]

	Decolorizer	Two-Stage non-selective abater
NO_x before reduction, ppm	3000	3000
NO_x after reduction, ppm	3000	300
Fuel	Natural Gas	Natural Gas
Investment, 10^3 $	60	255
$/scfm	2.60	11.00
Costs, 10^3 $/yr[a]		
Natural Gas	14	82
Ammonia	--	--
Catalyst	4	8
Steam	(50)	(144)
Investment-based costs[b]	30	128
Total Cost, 10^3 $/yr	(2)	74
Total Cost, $/ton HNO_3	(0.02)	0.75
Total Cost, $/ton NO_x removed	--	27

a) Parentheses indicate negative costs or savings

b) Includes 20 percent return before taxes

When purge gas is used the full cost is greatly decreased, but slightly lower combustor exit temperatures may decrease the steam yield and thus partially nullify the low fuel costs.

Catalyst investments are about $1.20 per scfm of tail gas or $100 per daily ton of product capacity.[18]

5.0 PLANTS CURRENTLY USING BEST TECHNOLOGY

While catalytic combustion devices have been used for about 15 years, very few plants have successfully achieved reductions of more than 80% for extended periods of time.

Nitric acid plants currently operating with very low reported emissions levels include:

Plant	Fuel Used	Approximate NO_x Emission Levels, ppm
DuPont, Repauno Plant Gibbstown, New Jersey	Natural Gas	300 - 500 ppm
Shell Chemical Co. St. Helen's Oregon	Ammonia Plant Purge Gas	100
Cresco Fertilizer Co. Western Port, Australia	Purge Gas	100

6.0 CURRENT REGULATIONS LIMITING NO_x EMISSIONS FROM NITRIC ACID PLANTS

The only regulations currently applied to nitric acid plants utilize the best feasible technology approach, equivalent opacity, and equivalent ambient air NO_x concentration at the plant property line. No regulations in the United States currently specify a quantitative emission value.

Equivalent opacity regulations while not strictly enforced, usually limit the emissions to 20 to 30% opacity.

Best feasible control technology is subject to varied interpretations depending on the type and age of the plant and its specific operating conditions. In West Germany an emission value of approximately 0.437 grains per $ft.^3$ (approximately 360 ppm) of total NO_x is indicative of good control practice. New Jersey's application of best control technology regulation is currently in the 300 - 500 ppm range.

The National Air Pollution Control Administration's Federal Facilities Division has set a maximum hourly property line ambient air NO_x concentration of 0.1 ppm for Federal Operations.[11] This value would apply to all operations at any one site; not just nitric acid plants.

7.0 RECOMMENDED EMISSION LEVELS FOR NEW PLANTS

The catalytic control techniques presently being applied to nitric acid plant tail gases are undergoing continual improvement and modification. Theoretically, with a sufficient supply of fresh catalyst, and enough excess fuel, a limit of zero NO_x can be approached. However, practicalities of design, economics, and fuel availability currently require a higher emission limitation for continued operation.

Based on the current level of technology the following emission limitations are recommended for <u>new</u> plants:

1) For plants able to use hydrogen or ammonia plant purge gas as a reducing fuel.

Total NO_x ($NO + NO_2$)	~~200~~ 100 to ~~300~~ 200 ppm	
NO_2	less than	10 ppm

Equivalent opacity = 0.

2) For plants using natural gas, propane, or similar hydrocarbon fuel.

Total NO_x ($NO + NO_2$	300 to 400 ppm	
NO_2		50 ppm

Equivalent opacity = 0.

Due to the changes taking place in emission control technology, these standards should be re-evaluated bi-annually.

REFERENCES

1. Bartok, W., et al., Systems Study of Nitrogen Oxide Control Methods for Stationary Sources. Esso Research and Engineering Co., Report, GR-2-NOS-69. NAPCA Contract PH-22-68-55. Vol. 1, Nov. 20, 1969, p. 1-4.

2. Newman, D. J., Pollution from Nitric Acid Plants, Presented at American Institute of Chemical Engineers Meeting, Denver, Colorado, Aug. 31, 1970. Chemico Co., New York, p. 2.

3. National Emission Standards Study, Senate Document 91-63, March, 1970, p. 87.

4. Gerstle, R. W. and R. F. Peterson, Atmospheric Emissions from Nitric Acid Manufacturing Processes. PHS Publication 999-A-27, 1966, p. 22-26.

5. Newman, D. J., Pollution from Nitric Acid Plants, Presented at American Institute of Chemical Engineers Meeting, Denver, Colorado, August 31, 1970, Chemico Co., New York, p. 11.

6. Personal Communication. E. Bingham, Farmers' Chemical Company, Harrison, Tennessee, September 3, 1970.

7. Anon. Nitric Acid: Smart Engineering Boosts the Yield. Chem. Eng., March 30, 1964, p. 38-40.

8. Personal Communication. H. Graham, Tennessee Valley Authority, Muscle Shoals, Alabama, August 31, 1970.

9. Brink, J. A., et al. Mist Removal from Compound Gases. Chemical Engineering, Prog. 62: 65, April, 1966.

10. Hardison, L. C., Techniques for Controlling the Oxides of Nitrogen, J. Air Pollution Control Association 20: 377-382. June, 1970.

11. Personal Communication, C. Maneri, NAPCA Federal Facilities Division, Deptember 2, 1970.

12. Newman, D. J., The Third Source: Pollution from Nitric Acid Plants. Presented at American Institute of Chem. Engineers, Denver, Colorado, August 31, 1970, p. 15-18.

REFERENCES (Continued)

13. Andersen, H. C., et al., A New Family of Catalysts for Nitric Acid Tail Gases. Engelhard Industries Technical Bulletin, VII (3): 100-105, December, 1966.

14. Hunter, J. B., Platinum Catalysts and System for Air Pollution Control, Part I, Matthey Bishop, Inc., Bulletin THT-3000.

15. Gerstle, R. W. and R. F. Peterson, Atmospheric Emissions from Nitric Acid Manufacturing Processes. PHS Publication 999-A-27, 1966, p. 22-26.

16. Romeo, P. L., Catalysts and the Control of Oxides of Nitrogen. Paper presented at Joint NAPCA, Army Munitions Command Seminar, Joliet, Illinois, June 3-5, 1970.

17. Anon. Catalyst Unit Cleans Up Nitrogen Oxide Stream. Chem. Eng., August 26, 1968, p. 38.

18. Bartok, W., et al., Systems Study of Nitrogen Oxide Control Methods for Stationary Sources. Esso Research and Engineering Co., Report, GR-2-NOS-69. NAPCA Contract PH-22-68-55. Vol II., Nov. 20, 1969, Chapter 6.

19. Personal Communication. Dr. D. Byrn, D. M. Weatherly Co., Atlanta, Georgia, September 3, 1970.